to be denied that many chemical reactions do take place instantaneously on the boundary of two phases, and a considerable number of interesting cases have been investigated by Brunner,* which evidently conform to this rule. It does not, however, seem probable that a useful purpose would be served in considering this rule to hold universally.

I have examined consequences drawn from it with regard to irreversible electrolytic reductions, and do not find them to agree with facts.† Many other cases might also be brought forward that would be very difficult to reconcile with this theory, *e.g.*, the great difference of velocity shown by metals in dissolving in different acids,‡ catalysis by substances such as nitrogen peroxide during the solution of copper in nitric acid, and others.

In conclusion, the author desires to say that he has had the advantage of discussing the matter treated in this paper with Dr. Senter and Professor Poynting, for which he acknowledges his indebtedness.

"On Galvanic Cells produced by the Action of Light. Preliminary Communication."§ By M. WILDERMAN, Ph.D., B.Sc. (Oxon). Communicated by Dr. LUDWIG MOND, F.R.S. Received November 8,—Read November 24, 1904.

(From the Davy-Faraday Laboratory of the Royal Institution.)

In my paper "On Chemical Statics and Dynamics" ('Phil. Trans.,' A, vol. 199, 1902, p. 337), and especially 'Zeit. Physik. Chemie,' vol. 42, 1902, pp. 316—335, I deduced, from thermodynamics, the laws experimentally found by me for velocity of chemical reaction, and for chemical equilibrium under the action of light, from the fundamental conception that the chemical potential of substance in light and in the dark is different, becoming greater in light. The foundation for this conception was that two metallic plates immersed in a liquid and connected to a circuit form a "galvanic" combination, when one plate is exposed to light while the other is kept in the dark; and, according to Gibbs' equation, $v'' - v' = \alpha_a(\mu_a' - \mu_a'')$, no galvanic cell could be formed, unless the chemical potentials at the two electrodes were different in light and in the dark.

The experiments of Becquerel and Minchin left students to infer

* 'Ztschft. Phys. Chem.,' vol. 47, p. 56 (1904).

† Faraday Society, October 25, 1904.

‡ Ostwald, 'Grundlinien d. anorganischen Chemie,' p. 249.

§ This paper contains a preliminary account of the author's further researches on "Chemical Statics and Dynamics of Reversible and Irreversible Systems under the Action of Light."

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that the E.M.F. observed is due to "surface phenomena," because, with AgCl, AgBr, AgI plates both observed currents sometimes in one direction, sometimes in the other, and in every experiment different curves and mysterious phenomena ("very curious cases of inversion of the current") were observed. No galvanic combination we know of gives a current in one direction at one time, in the opposite at another, the anode and cathode exchanging their parts.

Not only were the deflections of the galvanometer observed, but all the curves in all their complexity were studied and photographed from beginning to end, including the induction and deduction periods. I succeeded, after much trouble, in making the investigation quantitative instead of qualitative, as hitherto; the results observed were studied, and considered in connection with the chemical composition of the heterogeneous system, and with those chemical reactions, previously unknown to us, which take place in the different systems under the action of light; the complex nature of the phenomena observed was found, quantitatively separated into constituents, and freed from interfering concomitants, etc.

Though the ampères and volts measured were mostly exceedingly small (the first had to be measured in units of 10^{-9}, and the second in units of 10^{-6}), the photographed curves obtained show that the experimental difficulties in this region were quite overcome, since concordant results were obtained on repetition of the experiments.

As the result of more than 3 years' work, I find that there is, under the action of light, a region of galvanic cells as wide and as varied as in the case of ordinary galvanic cells. We have here constant and inconstant cells, reversible and irreversible cells. The chemical reactions and chemical equilibrium in these galvanic combinations are now perfectly clear, yet they are all *sui generis*, all the phenomena being intermixed, and characterised by phenomena of induction and deduction peculiar to light cells only. I succeeded also in placing this region of phenomena on a physico-mathematical basis, testing and proving the equations experimentally in all details. The principal results obtained are:—

(1) The total E.M.F. produced by light consists of an E.M.F. produced by light at a constant temperature, owing to increase of chemical potential, and of solution pressure of the exposed plate, and of a thermo-E.M.F. caused by one of the two plates in contact with the liquid being heated by light. Both E.M.F.'s are found to be directly proportional to the intensity of light, and both give currents in the same direction, proving that light acts on chemical potential, as well as on solution pressure of the electrode, in the same way as does heat. My generalisation for light: "Each kind of equilibrium between two states of matter (system) is, at constant volume, on exposure to light, shifted in the direction accompanied by greater absorption of light"

(analogous to van't Hoff's "principle of moveable equilibrium" for heat) is thus proved.*

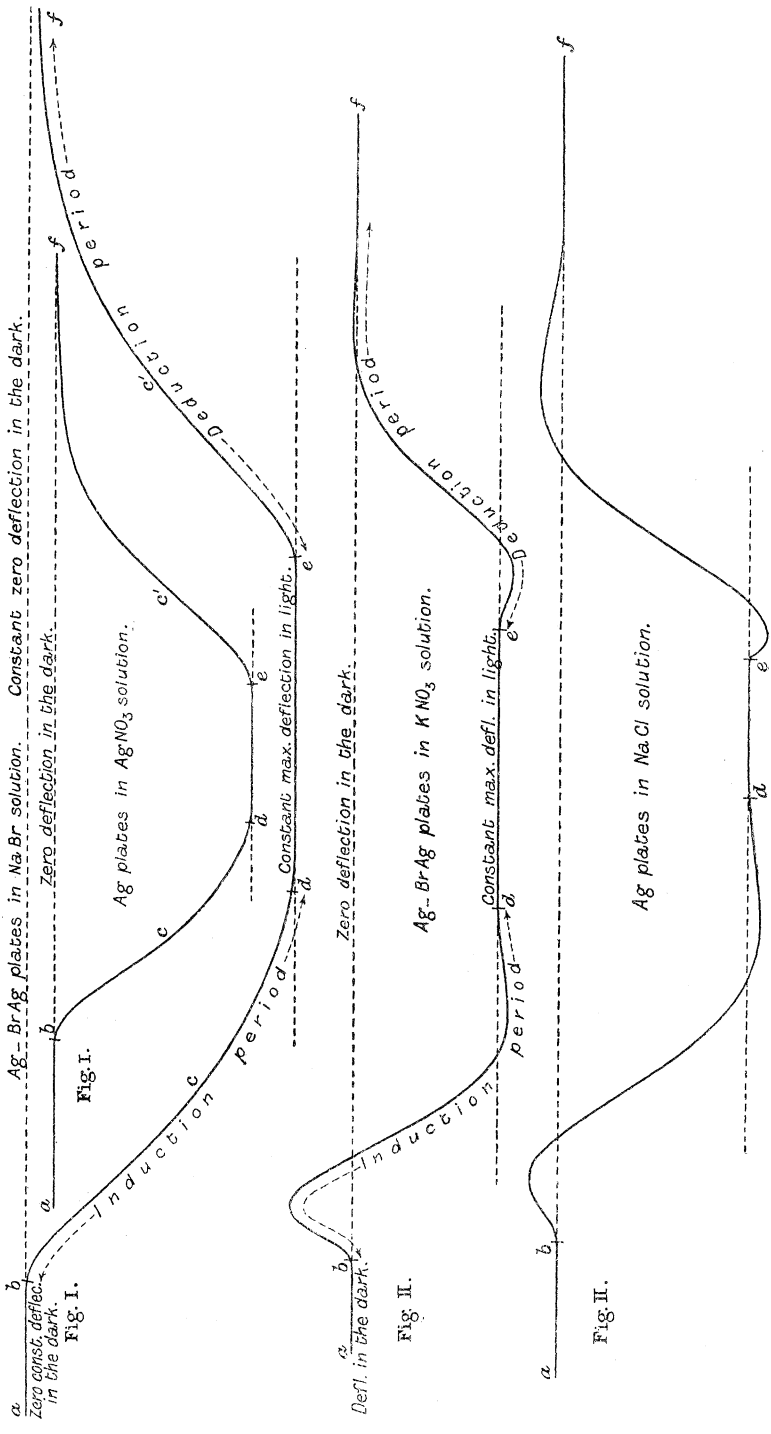
(2) The phenomena of reversal of the current, etc., observed by Becquerel and Minchin, are due, not to surface phenomena or different "thicknesses of sensitive layer," but to the fact that their combinations all give inconstant cells showing polarisation, a phenomenon which they and other observers entirely overlooked, since they made no study of the induction and deduction periods. Whenever a consideration of the composition of the heterogeneous system, and of the reactions going on in the same under the action of the current, shows that an inconstant cell should be formed, the curve illustrated by fig. 2 is obtained, the peculiar course of the induction and deduction periods being caused by the principal E.M.F. and the E.M.F. of polarisation being set up simultaneously under the action of light, with different velocities, and diminishing on removal of the light, with different velocities, vanishing almost simultaneously. Whenever a consideration of the composition of the heterogeneous systems, and of the reactions going on in the same under the action of the current, shows that the cell should be reversibly constant, then, provided the action of light upon the plate is such as to allow of the formation of a constant cell, and, provided the plates are so prepared as to avoid the formation of "gas batteries" (for this the E.M.F. in the dark must be made very small—a few millionths of a volt) we get constant cells, the induction and deduction period having a normal course, as illustrated in fig. 1.

(3) The law governing the induction period in constant reversible cells is evidently

$$\frac{d\pi}{d\tau} = c\,(\pi_0' - \pi)\,(\pi - \pi_0 + \mathrm{K}),$$

i.e., the speed with which the system approaches, on exposure to light, its new state of equilibrium in light (given by the line *d*—*e*, and characterised by the value of constant E.M.F., π_0') is directly proportional to the remoteness of the system at the given time, τ, from the point of equilibrium in light (given by the value $\pi_0' - \pi$, if π is the E.M.F. at the time τ, while π_0' is the maximum E.M.F. in light), and to the amount of variation already produced by light in the system up to the time τ (given by $\pi - \pi_0$, if π_0 is the initial E.M.F. of the system in the dark) plus a constant K, which is also of the character of an instability constant, *i.e.*, the more the system is removed from its point of equilibrium in light, the quicker it approaches it, and the more the molecules and atoms have been shaken up by light (exposed to light previously to the time τ), the quicker the system approaches the point of equilibrium in light. This gives also the fundamental law of photography, the connection between the amount of silver salts decomposed and the time of exposure, since the E.M.F. is, during this

* See 'Zeitsch. physik. Chemie,' 1902, p. 332; 'Phil. Mag.,' 1903, vol. 5, p. 223.


Ag – Br Ag plates in Na Br solution.
Constant zero deflection in the dark.
Zero deflection in the dark.
Ag plates in $AgNO_3$ solution.
Constant max. deflection in light.
Induction period
Reduction period
Zero const. deflec. in the dark.
Fig. I.
Fig. I.
Zero deflection in the dark.
Ag – Br Ag plates in KNO_3 solution.
Constant max. defl. in light.
Induction period
Reduction period
Defl. in the dark.
Fig. II.
Ag plates in Na Cl solution.
Fig. II.

period, directly proportional to the current, and gives the true measure of the amount of silver salts decomposed by light. The equation for the deduction period is also

$$-\frac{d\pi}{d\tau} = -c'(\pi_0 - \pi)(\pi - \pi_0' + K'),$$

i.e., is directly proportional to the remoteness of the system from the point of equilibrium in the dark, $\pi_0 - \pi$, and to $\pi - \pi_0'$, which gives the amount of variation produced by the removal of the light in the system already, up to the time τ plus a constant K′.

(4) The physico-mathematical theory of "constant cells reversible in respect of the cation" (*e.g.*, Ag plate in light, $AgNO_3$ solution in light, $AgNO_3$ solution in dark, Ag plate in dark) is the following. The result of the process under the action of light consists :—

(1) In one gramme-atom of the cation $(\overset{+}{Ag})$ of a higher chemical potential passing from the electrode (Ag) in light into the solution of the salt of the electrode in light.

(2) From the solution in light the gramme-atom of the cation passes to the solution in dark, transforming there into cations of a lower chemical potential, passing a deduction period.

(3) Finally from the solution in dark the gramme-atom of the lower chemical potential separates upon the electrode (Ag) in dark.

Let the solution pressure of the plate be in dark P_d, the osmotic pressure of the cations (+Ag) in the solution in dark p_d. Then, since the chemical potential of a substance is different (greater) in light than in dark, the solution pressure of the same plate in light will be P_l, and the osmotic pressure of the cations of the same concentration in light will be p_l. If now we calculate the work done by such a system, when, under the action of light, 1 gramme-atom of Ag passes from the plate in light to the plate in dark, we get

for (1) $$E_1 = 0{\cdot}860T \log_e \frac{P_l}{p_l} . 10^{-4} \text{ volt};$$

for (2) $$E_2 = 0{\cdot}860T \frac{u-v}{u+v} \log_e \frac{p_l}{p_d} . 10^{-4} \text{ volt (very nearly)};$$

for (3) $$E_3 = 0{\cdot}860T \log_e \frac{P_d}{p_d} . 10^{-4} \text{ volt};$$

and

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860T \left(\log_e \frac{P_l}{P_d} - \frac{2v}{u+v} \log_e \frac{p_l}{p_d}\right) 10^{-4} \text{ volt} \quad \text{(I)}$$

gives the value of the E.M.F. of such combinations under the action of light. This equation shows :—

(1) The E.M.F. of such a combination must be independent of concentration, *i.e.*, $\Sigma E - \Sigma E' = 0$.

This was found experimentally to be the case.

(2) Experiments were made which showed that both the value

$$0{\cdot}860\,\mathrm{T}\,\frac{2v}{u+v}\log_e\frac{p_l}{p_d}\,.\,10^{-4}\text{ volt}$$

and the electrical potential difference between the illuminated and the non-illuminated solution can be neglected, in comparison with the electrical potentials of the plates and solution. Thus Equation (I) can be written

$$\Sigma\mathrm{E} = 0{\cdot}860\,\mathrm{T}\left(\log_e\frac{\mathrm{P}_l}{\mathrm{P}_d}\right)10^{-4}\text{ volt} \quad\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(IV).}$$

(3) Since P_l is $>\mathrm{P}_d$, $\Sigma\mathrm{E}$ is positive, *i.e.*, the current must flow from the plate in light to the plate in dark, as was actually found.

(4) From $\Sigma\mathrm{E} = 0{\cdot}860\,\mathrm{T}\log_e\frac{\mathrm{P}_l}{\mathrm{P}_d}\,.\,10^{-4}$ volt or $\epsilon_0\Sigma\mathrm{E} = \mathrm{RT}\log_e\frac{\mathrm{P}_l}{\mathrm{P}_d}$, we get on differentiating and putting $\frac{d\mathrm{P}_d}{d\mathrm{T}} = \frac{-\rho+\mathrm{RT}}{\mathrm{T}v}$, $\frac{d\mathrm{P}_l}{d\mathrm{T}} = \frac{-\rho'+\mathrm{RT}}{\mathrm{T}v}$ (where ρ and ρ' are the heat of transformation of Ag into $\overset{+}{\mathrm{A}}\mathrm{g}$ ions in light and in dark), a law, analogous to that of Gibbs and Helmholtz for ordinary galvanic cells:

$$\epsilon_0\Sigma\mathrm{E} = \rho'' + \frac{\epsilon_0 d\Sigma\mathrm{E}}{d\mathrm{T}}\,.\,\mathrm{T} \quad\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(VI).}$$

(5) Equation (VI) allows us to calculate the heat of reaction (ρ'') from the E.M.F.s observed; ρ and ρ', or the heat of transformation of Ag into $\overset{+}{\mathrm{A}}\mathrm{g}$ cations must evidently be different in light and in dark.

(6) By Equation (IV) we can calculate both the ratio of the two solution pressures of the same electrode in light and in dark, from the E.M.F. observed, and also the absolute value of P_l if P_d is known otherwise.

(7) It was found experimentally that the E.M.F. created by light, or the work done by the system under the action of light, is directly proportional to the intensity of light.*

(5) The physico-mathematical theory of "constant cells reversible in respect of the anion" (*e.g.*, Ag-BrAg plate in light, KBr solution in light, KBr solution in dark, Ag-BrAg plate in dark) is the following.

The result of the process under the action of light consists of:—

(1) One gramme-atom of the anion ($\overset{-}{\mathrm{B}}\mathrm{r}$) of a higher chemical potential passes from the electrode Ag-BrAg in light into the solution containing a salt of the same acid (BrK) as the salt (BrAg) covering the metal plate Ag.

(2) The gramme-atom of the $\overset{-}{\mathrm{B}}\mathrm{r}$ ions passes from the solution in light to the solution in dark, transforming into anions of a lower chemical potential; and

(3) The gramme-atom of the $\overset{-}{\mathrm{B}}\mathrm{r}$ ions in the dark of the lower chemical potential separates from the solution upon the electrode in the dark.

If we now calculate the maximum work done by such a system, when under the action of the current 1 gramme of anion ($\overset{-}{\mathrm{B}}\mathrm{r}$) passes from the plate in light to the plate in dark, putting P_l, P_d, for the solution

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* See 'Zeitsch. physik. Chemie,' 1902, pp. 319 and 333; 'Phil. Mag.,' 1903, vol. 5, pp. 211, 224.

pressures of the electrodes in respect of the anion in light and in dark and p_l and p_d for the osmotic pressures of the anions in light and in dark, we get

for (1) $$E_1 = 0{\cdot}860T \log_e \frac{p_l}{P_l} . 10^{-4} \text{ volt};$$

for (2) $$E_2 = 0{\cdot}860T \frac{u-v}{u+v} \log_e \frac{p_l}{p_d} . 10^{-4} \text{ volt (approximately)};$$

for (3) $$E_3 = 0{\cdot}860T \log_e \frac{p_d}{P_d} . 10^{-4} \text{ volt};$$

and

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860T\left(-\log_e \frac{P_l}{P_d} + \frac{2u}{u+v} \log_e \frac{p_l}{P_d}\right) 10^{-4} \text{ volt}, \quad \text{(I)}.$$

This is the general equation. It follows:—

(1) The E.M.F. must be independent of concentration; and this was actually found by direct experiment.

(2) An experimental investigation of the value $0{\cdot}860\,T \frac{2u}{u+v} \log_e \frac{p_l}{p_d} 10^{-4}$ volt and of the electrical potential difference between the illuminated and not illuminated solution showed in two different ways that it can be neglected, so that we can put

$$\Sigma E = 0{\cdot}860\,T . \log_e \frac{P_d}{P_l} . 10^{-4} \text{ volt} \ldots\ldots\ldots\ldots\ldots \quad \text{(IV)}.$$

(3) Equation (IV) shows that, since $P_l > P_d$, the current must flow from the plate in the dark to the plate in the light, as was found experimentally.

(4) The connection is deduced, from Equation (IV), between the E.M.F. of a constant galvanic combination reversible in respect of the anion under the action of light and the heat of chemical reaction in the same, or the chemical energy created by light:

We have

$$\Sigma E = 0{\cdot}860\left(\log_e \frac{P_d}{P_l} + \frac{2u}{u+v} \log_e \frac{p_l}{p_d}\right) 10^{-4} \text{ volt} = 0{\cdot}860\,T \log_e \frac{P_d}{P_l} . 10^{-4} \text{ volt},$$

or $$n_e \varepsilon_0 \Sigma E = RT \log_e \frac{P_d}{P_l}, \text{ and for } n_e = 1,\ \varepsilon_0 \Sigma E = RT \log_e \frac{P_d}{P_l}.$$

From this equation we get

$$n_e \varepsilon_0 \Sigma E = RTd\left(\log_e \frac{P_d}{P_l}\right) + R \log_e \frac{P_d}{P_l} \frac{dT}{T} = RTd\left(\log_e \frac{P_d}{P_l}\right) + n_e \varepsilon_0 \Sigma E \frac{dT}{T}.$$

Now the solution pressures must follow in light and in dark a law similar to Clausius' law of evaporation, and $\frac{d}{dT}\left(\log_e \frac{P_d}{P_l}\right) = \frac{\rho''}{RT^2}$; therefore

$$RTd\left(\log_e \frac{P_d}{P_l}\right) = \rho'' \frac{dT}{T}, \quad \text{and} \quad n_e \varepsilon_0 \Sigma E = \rho'' + \frac{n_e \varepsilon_0 d\Sigma E}{dT} . T \ldots \quad \text{(VI)},$$

i.e., we get for constant galvanic cells reversible in respect of the anion in light, a law analogous to that of Gibbs and Helmholtz and according as $\frac{n_e \varepsilon_0 d\Sigma E}{dT}$ is $>$, $=$ or $< \rho''$, the system will take up or not, or give up heat to the surrounding medium.

(5) Equation (VI) allows us to calculate the heat of reaction in galvanic combinations created by light, from the observed E.M.F. and its temperature coefficient. The much greater deflections obtained here induced the author to make vigorous efforts to determine the temperature coefficient of the E.M.F. observed, but the enormous experimental difficulties entailed prevented him from getting more than the general result that it can only be very small (experiments with KBr solutions and LiBr solutions). For the same reason the heat of reaction can be determined only approximately.

(6) As to the solution tension in light and in dark, there are differences between cells created by light and ordinary galvanic cells; the first are dependent upon the capacity of absorption of light, the effect of previous illumination, physical changes in the dark, the intensity of light, etc.; all this makes the solution tension of an electrode in light *sui generis*, distinct from the solution tension of ordinary galvanic cells.

(7) The E.M.F. of constant cells reversible in respect of the anion is found also to be directly proportional to its intensity ($\Sigma E = c \,.\, I$ (VII)). Since the light energy falling upon the plate is also directly proportional to the intensity of light, *i.e.*, $L = K \,.\, I$, we have $\Sigma E = \frac{c}{K} L$, *i.e.*, the E.M.F. or the work done by the given system forms always the same fraction of the total light falling upon it, and this must hold good for monochromatic light as well. Since the solution pressure of a substance in the dark is a constant, it follows from (VII) that

$$-\log_e P_l = c \,.\, I : 0{\cdot}860\, T \,.\, 10^{-4} - \log_e P_d \quad \text{and} \quad \log_e P_l = K'' \,.\, I + K''' \quad \text{(VIII)}.$$

This equation gives the variation of the solution pressure P_l of the electrode in light in dependence upon its intensity; if P_d is known from other sources the absolute value of P_l can be calculated for each intensity of light from (VIII).

(6) The theory of thermogalvanic cells is the following. An analysis of the chemical reactions going on in such systems (two equal plates immersed in a solution, one plate being kept at a higher temperature than the other) shows that, *e.g.*, Ag plates in $AgNO_3$ solution must form a constant cell reversible in respect of the cation, that Ag-BrAg plates in NaBr solution must form constant cells reversible in respect of the anion, and Ag plates in NaCl solution must give an inconstant irreversible combination, etc.

The E.M.F. of a thermogalvanic combination evidently consists of: (1) The potential difference between one of the plates and the solution at $T_{,}$, (2) the potential difference of the same plate and the same solution at $T_{,,}$ and (3) the potential difference between two solutions of the different temperatures, *i.e.*, $\Sigma E = E_1 - E_2 + E_3$.

Now we have for the single electrical potential differences $E_1 = \rho + \frac{dE}{dT} T_{,}$ at $T_{,}$, $E_2 = \rho + \frac{dE}{dT} T_{,,}$ at $T_{,,}$ where ρ is the heat of ionisation of one gramme-atom of ions ($\overset{+}{Ag}$ in the above mentioned constant cell reversible in respect of the cation), while E_3 can be put $= E' (T_{,} - T_{,,})$, *i.e.*, the force driving the ions from one part of the solution at one temperature to the other part of the solution at another temperature must be directly proportional to the difference of the two temperatures,

because the osmotic pressures are $p_1 = \frac{RT_{,}}{v}$, $p_2 = \frac{RT_{,,}}{v}$ and $p_1 - p_2 = \frac{R}{v}(T_{,} - T_{,,})$. Therefore

$$\Sigma E = \left(\frac{dE}{dT} + E'\right)(T_{,} - T_{,,}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (I),$$

i.e., the E.M.F. of thermogalvanic cells must be directly proportional to the difference of temperature of the two electrodes, a law which is analogous to the thermo-E.M.F. produced when two metals are in contact, instead of a metal and solution. (The assumption, however, is made that ρ or heat of ionisation can be taken between $T_{,}$ and $T_{,,}$ to remain constant.)

The laws for thermogalvanic cells can be deduced in another way from the solution pressures of the electrodes and the osmotic pressures of the solution. We take the system (Ag, NO_3Ag sol.)$T_{,}$ (NO_3Ag sol., Ag)$T_{,,}$.

We have

$$E_1 = 0{\cdot}860 T_1 \log_e \frac{P_{T_{,}}}{p_{T_{,}}} . 10^{-4} \text{ volt}; \quad E_2 = 0{\cdot}860 T_{,,} \log_e \frac{P_{T_{,,}}}{p_{T_{,,}}} . 10^{-4} \text{ volt};$$
$$E_3 = E'(T_{,} - T_{,,});$$

and

$$\Sigma E = E_1 - E_2 + E_3$$
$$= 0{\cdot}860 \left(T_{,} \log_e \frac{P_{T_{,}}}{p_{T_{,}}} - T_{,,} \log_e \frac{P_{T_{,,}}}{p_{T_{,,}}}\right) 10^{-4} \text{ volt} + E'(T_{,} - T_{,,}) \quad \ldots\ldots\ldots\ldots \quad (I),$$

where $P_{T_{,}}$, $P_{T_{,,}}$ are the solution pressures of the silver electrodes at $T_{,}$ and $T_{,,}$. Similarly we get for cells reversible in respect of the anion

$$\Sigma E = 0{\cdot}860 \left(T_{,} \log_e \frac{p_{T_{,}}}{P_{T_{,,}}} - T_{,,} \log_e \frac{p_{T_{,,}}}{P_{T_{,,}}}\right) 10^{-4} \text{ volt} + E_1'(T_{,} - T_{,,}) \ldots (II).$$

Since $p_{T_{,}}$, $p_{T_{,,}}$ are directly proportional to the absolute temperature, we have for systems reversible in respect of the cation

$$p_{T_{,}} = a\mu T_{,}, \qquad p_{T_{,,}} = a\mu T_{,,},$$

and

$$\Sigma E = 0{\cdot}860 (T_{,} \log_e P_{T_{,}} - T_{,,} \log_e P_{T_{,,}}) 10^{-4} \text{ volt}$$
$$+ 0{\cdot}860 (T_{,,} \log_e a\mu T_{,,} - T_{,} \log_e a\mu T_{,}) 10^{-4} \text{ volt} + E'(T_{,} - T_{,,}) \ldots \quad (I'),$$

and for systems reversible in respect of the anion,

$$\Sigma E = 0{\cdot}860 (T_{,,} \log_e P_{T_{,,}} - T_{,} \log_e P_{T_{,}}) 10^{-4} \text{ volt}$$
$$+ 0{\cdot}860 (T_{,} \log_e a\mu T_{,} - T_{,,} \log_e a\mu T_{,,}) 10^{-4} \text{ volt} + E_1'(T_{,} - T_{,,}) \ldots \quad (II').$$

Equation (II′) differs from the equation of Nernst by the term E_3 which I put $= E_1'(T_{,} - T_{,,})$, but while Nernst assumes that E_1 and E_3 remain unknown, and tries to eliminate them (*i.e.* their content), by the use of two different concentrations, we shall try to determine the value and content of these equations so as to get to the fundamental equation concerning the thermogalvanic system for any one concentration.

If $P_{T_{,}}$ and $P_{T_{,,}}$ are the solution pressures of the electrodes, they must follow a law analogous to Clausius' law for evaporation in a vacuum, *i.e.*,

$$\frac{dP}{dT} = \frac{-\rho + RT}{Tv} \quad \text{and therefore} \quad \log_e P_{T_{,}} = \frac{\rho}{RT_{,}} + \log_e T_{,} + K$$

and $\log_e P_{T_{,,}} = \frac{\rho}{RT_{,,}} + \log_e T_{,,} + K.$

Putting these values into equation I and II′ we get :—

$$\Sigma E = [0{\cdot}860\,(K - \log_e a\mu)10^{-4} + E']\,(T_{,} - T_{,,}), \text{ instead of (I′)};$$

$$\Sigma E = [0{\cdot}860\,(\log_e a\mu - K')\,10^{-4} + E']\,(T_{,} - T_{,,}), \text{ instead of (II′)},$$

i.e., the E.M.F. of constant thermogalvanic cells reversible in respect of either cation or anion, must be directly proportional to the differences of temperature of the two plates in contact with the liquid. From the observations of Nernst and myself, it can be shown that this is actually the case. Hence we prove that:

(1) The thermogalvanic E.M.F. is directly proportional to the difference of temperature of the two places of contact of the plates with the liquid (deduced in two ways).

(2) The solution pressure of the electrodes follows a law similar to Clausius' law of evaporation.

(3) The law of Gibbs and Helmholtz giving the connection between the E.M.F. of a galvanic combination, the heat of reaction, and the temperature coefficient of the E.M.F., holds good for each of the two potentials separately, giving thus the connection between the electric potential differences of the given plate and solution, the heat of ionisation of the given plate, and the temperature coefficient of the value of this potential difference.

(7) A very detailed investigation of the E.M.F. in the dark showed that it is due to the formation of "gas batteries" through adhesion of gases in different concentrations to the plates, the degree of adhesion depending upon the state of the surface of the plate. The current polishes the plates, the amount of the gases adhering to them becomes thus more equal, and according to the equation $\pi = \frac{0{\cdot}0002T}{n_e} \log_e \frac{P_1}{P_2}$ the E.M.F. of the gas battery becomes smaller. From these we must distinguish gas batteries created under the action of light as the result of the chemical processes going on in the system under the action of the current—the separation of gas upon one electrode only, or of different gases on the two electrodes.